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Internal Phosphorus Loading in Lake Pepin (Minnesota-Wisconsin)

by   William F. James, John W. Barko, Harry L. Eakin

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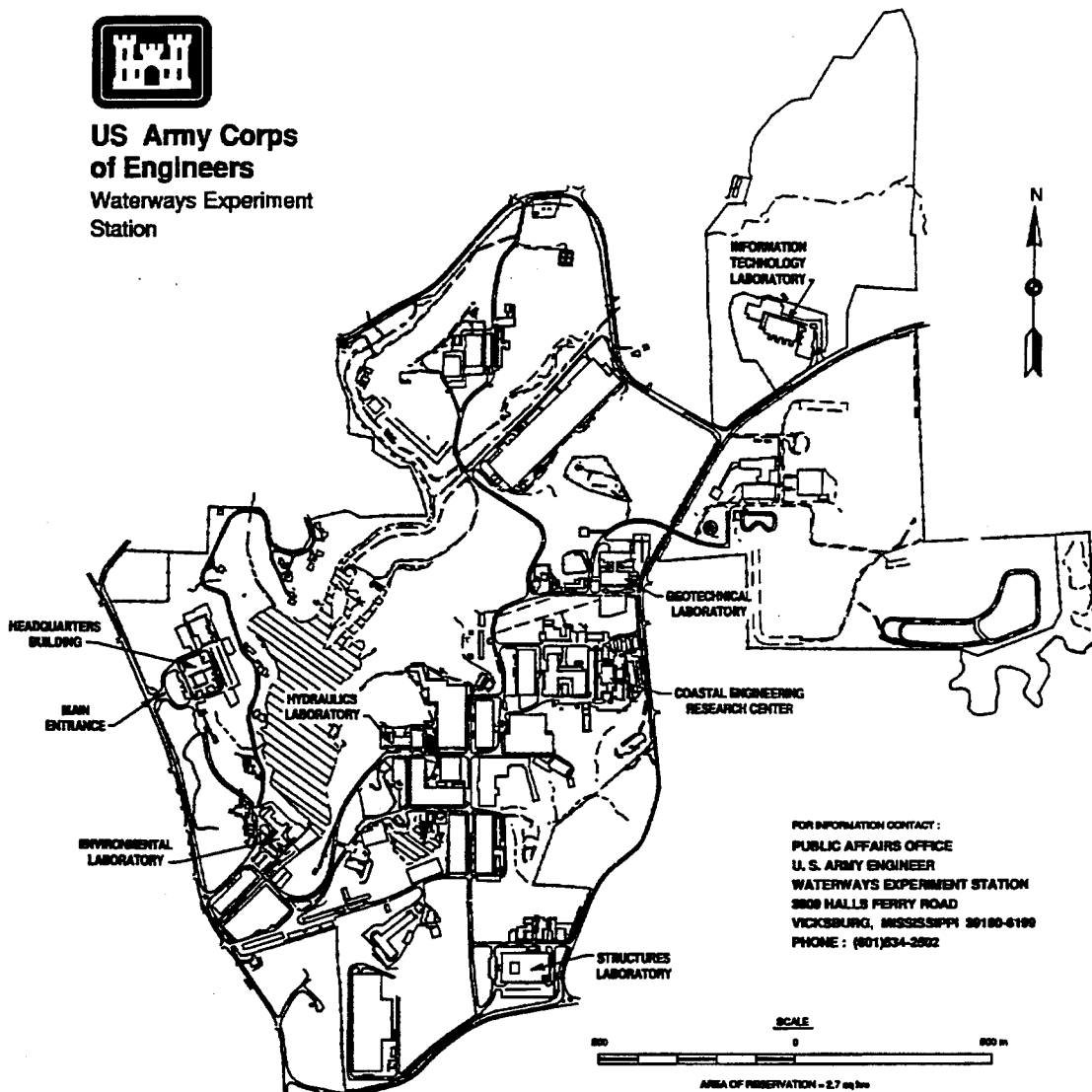3909 Halls Ferry Road
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Final report

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STRUCTURES
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SCALE

AREA OF RESERVATION = 2.7 sq km

Contents

Preface

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1 Introduction

Assessments of phosphorus (P) loadings are essential for determining the trophic state of lakes and reservoirs and potential management alternatives. Historically, these assessments have focused primarily on external P loading from the watershed (Vollenweider 1976) and internal P loading from anoxic hypolimnia (Nürnberg 1984). Increasing concerns over deteriorating water quality and accelerated eutrophication of Lake Pepin, a natural impoundment located on the upper Mississippi River, have led to a detailed examination of external P loadings and point source P contributions from the watershed (Minnesota Pollution Control Agency 1993a and b, Lung and Larson 1994). One P control measure presently under consideration is the reduction of point source P loads from the Metropolitan Wastewater Treatment Plant (Lung and Larson 1994), located 50 miles upstream of Lake Pepin in St. Paul, MN. The treatment plant accounts for about 20 percent of the mean total external P load to the lake (Minnesota Pollution Control Agency 1993a).

Internal P loading from sediments can often delay lake recovery substantially following reductions in external P loading (Welch 1977, Larson et al. 1979, Ryding 1981). This is an important concern in evaluating P reduction measures for Lake Pepin. While internal loading via P release from anoxic sediments has been well documented (Nürnberg 1984, 1987), little is known about the role of P release from sediments under oxic conditions. While most lake restoration efforts have ignored the potential for P release from sediments under oxic conditions, there is strong evidence that even oxic sediments can contribute substantially to the P economy of lakes (Drake and Heaney 1987, James and Barko 1991). P release from sediments under oxic conditions may be a very important component of the P budget of Lake Pepin, which stratifies thermally only intermittently during the summer.

Rates of P release from the sediments of Lake Pepin are estimated based on results of laboratory studies conducted under controlled redox and temperature conditions. These rates are compared with diffusional fluxes of P calculated from in situ profiles of P in the porewater. Finally, different sediment P pools and correlations with P release from the sediment are examined. The objective is to evaluate the importance of internal P loading from oxic as well as anoxic sediment as components of the P budget of Lake Pepin.

2   Methods

Intact cores were collected under the ice during the winter of 1992 for the determination of rates of soluble reactive P (SRP) release from sediments in Lake Pepin. Six replicate cores were collected from each of 12 stations situated along both longitudinal and depth gradients in the lake (Figure 1). A Wildco KB sediment core sampler (Wildco Wildlife Supply Co.), equipped with an acrylic core liner (6.5-cm inside diameter and 50-cm length), was used to collect sediment. Additional lake water was collected within 0.50 m of the sediment surface at each site for incubation with the collected sediment.

LAKE PEPIN

Upper Mississippi River

Legend

■ Lab P Release, Peepers, and Sediment P Fractions

● Lab P Release and Sediment P Fractions
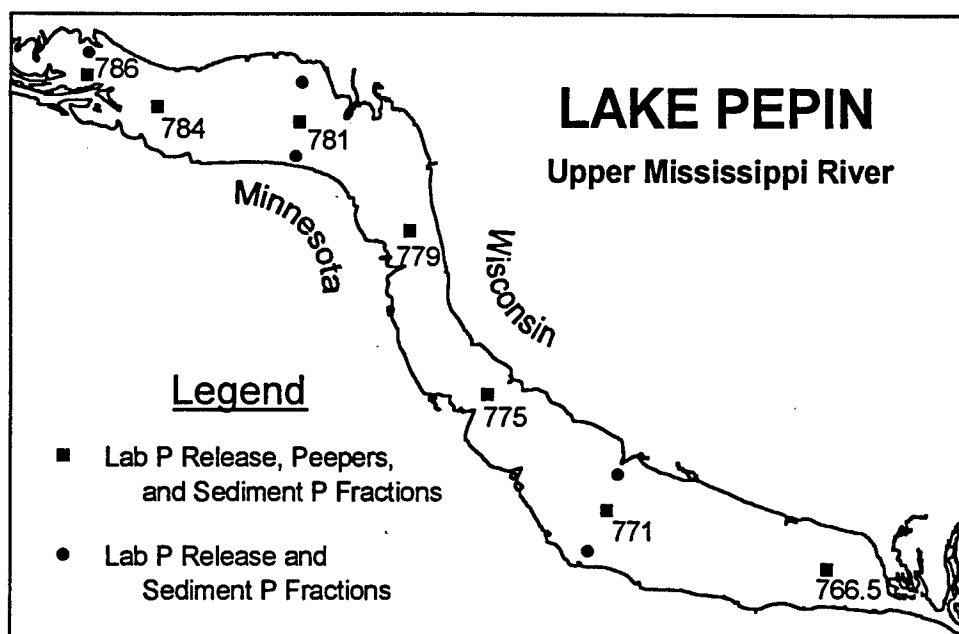
Figure 1.   Sampling locations in Lake Pepin

Sediment systems, constructed according to the methods of James and Barko (1991), were incubated in an environmental chamber at 25 °C for 1 to 2 weeks. This incubation temperature was chosen to simulate average temperature conditions near the bottom in Lake Pepin during the summer months (late June through August). One set of three replicate sediment incubation systems was subjected to an oxic environment while the other set (three replicates) was subjected to an anoxic environment for each station. The

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oxidation-reduction environment in each system was controlled by gently bubbling either air (oxic) or nitrogen (anoxic) through an air stone placed just above the sediment surface. Bubbling action ensured complete mixing of the water column but did not disrupt or resuspend the sediment. An equilibrium pH of either 8.3, for oxic conditions, or 9.0, for anoxic conditions, was achieved via air and nitrogen bubbling, respectively. These ranges in pH are commonly observed in Lake Pepin (see Chapter 3). Water samples were collected daily from the overlying water of each sediment system, filtered through a 0.45-μm membrane filter, and analyzed colorimetrically for SRP using the ascorbic acid method (American Public Health Association (APHA) 1985). Rates of SRP release from the sediment (mg m^{-2} day^{-1}) were calculated as linear changes in P mass in the overlying water (corrected for dilution effects due to daily replacement of lake water) divided by time and the area of the incubation system.

In conjunction with the P release measurements, three additional surficial sediment samples were collected at each station for determination of total and extractable sediment P. The upper 10 cm of the surficial sediment was immediately extruded into an airtight container and sealed to preserve the redox integrity of the sediments. In the laboratory, sediments were gently homogenized under a nitrogen atmosphere prior to P fractionation. Analyses of total sediment phosphorus concentrations (P-TOTAL) were performed colorimetrically using Technicon Auto-analyzer II procedures (Technicon Industrial Systems 1978, APHA 1985) following digestion with sulfuric acid, potassium sulfate, and red mercuric oxide (Plumb 1981). Sequential fractionation of inorganic P in the sediments was conducted according to Hieltjes and Lijklema (1980) for the determination P-NH$_4$Cl (i.e., interstitial P, loosely bound P, and CaCO$_3$-adsorbed P), P-NaOH (i.e., iron- and aluminum-bound P), and P-HCl (i.e., calcium-bound P). Each extraction was filtered through a 0.45-μm filter under a nitrogen environment, adjusted to pH 7, and analyzed for SRP. All sediment concentrations are expressed in units of mg g^{-1} dry sediment mass.

During July through early August of 1992, three replicate sediment peepers, similar to those described by Shaw and Prepas (1989), were placed in the sediments at five stations in Lake Pepin (Figure 1) to examine in situ Fickean diffusional fluxes and vertical gradients in P at the sediment-water interface via dialysis techniques. Methods of sediment peeper preparation and deployment are described in James and Barko (1991). Samples collected after 14 days of deployment were analyzed for SRP. Fickean diffusional fluxes (J, mg m^{-2} day^{-1}) of P across the sediment-water interface were calculated as:

$$J = -\Phi \times D \times \Theta^{-2} \times \frac{dC}{dx}$$

(1)

(Berner 1980),

where

Φ = porosity of the sediment (0.70)

D = areal sediment diffusion coefficient at 25 °C (7.50×10^{-5} cm^2 sec^{-1} (Li and Gregory 1974)

Θ^{-2} = tortuosity of the sediment (1.50; estimated from Sweerts et al. 1991)

dC/dx = SRP gradient across the sediment-water interface

Sediment cores were collected at each site for the determination of sediment porosity. Sediment porosity was calculated as the water mass in the upper 2 cm divided by the volume of the core section. Gradients in SRP were calculated from concentrations immediately above and below (2-cm interval) the sediment-water interface. In conjunction with the retrieval of the sediment peepers, water temperature, dissolved oxygen, and pH were determined at 0.5-m depth intervals at these same stations using a Hydrolab Surveyor II that was precalibrated against Winkler titrations and buffer solutions.

3 Results and Discussion

Over all stations, the mean rate of P release from sediments in Lake Pepin was greater under anoxic than oxic conditions (Table 1). The mean rate of P release (15.0 mg m^{-2} day^{-1}) from anoxic sediments in Lake Pepin was very similar to rates of P release from anoxic sediment estimated by Nürnberg et al. (1986) for a variety of eutrophic lakes. The dominant inorganic P fractions in the sediments of Lake Pepin were P-NaOH followed closely by P-HCl (Table 1). P-NH$_4$Cl constituted only 10 percent of the measured total inorganic P fraction, indicating that most of the inorganic P in the sediments was associated with the iron, aluminum, and calcium. In general, the total inorganic P fraction accounted for nearly 70 percent of P-TOTAL. Mean P-TOTAL and P-NaOH were significantly lower, while mean P-NH$_4$Cl and P-HCl were not significantly different (t-test, Statistical Analysis System (SAS) Institute 1985) from the means estimated for 66 lakes in eastern North America (Ostrofsky 1987).

Table 1
Simple Statistics for Various Sediment Characteristics In Lake Pepin (n = 30-36)

Variable	Mean	Standard Deviation	Minimum Value	Maximum Value
Oxic P release, mg m^{-2} d^{-1}	3.8	2.1	1.9	9.3
Anoxic P release, mg m^{-2} d^{-1}	15.0	4.1	8.6	24.0
P-TOTAL, mg g^{-1}	0.97	0.32	0.52	1.60
P-NH$_4$CL, mg g^{-1}	0.07	0.04	0.01	0.17
P-NaOH, mg g^{-1}	0.30	0.23	0.06	1.28
P-HCl, mg g^{-1}	0.28	0.17	0.08	0.61

Significant ($p < 0.05$) correlations existed among many of the chemical variables measured for the surficial sediments of Lake Pepin; however, Pearson correlation coeffients (r) were generally low (Table 2). P-TOTAL was positively correlated with P-NH$_4$Cl and P-NaOH, but negatively correlated with

Table 2
Pearson Correlation Coefficients (r) for Oxic Sediment
P Release Rates (mg m^{-2} d^{-1}; Oxic), Anoxic Sediment P Release
Rates (mg m^{-2} d^{-1}; Anoxic), Sediment Total P (mg/g; P-TOTAL),
NH$_4$CL-extractable P (mg/g; P-NH$_4$Cl), NaOH-extractable P (mg/g;
P-NaOH), and HCl-extractable P (mg/g; P-HCl)

	Anoxic	P-Total	P-NH$_4$Cl	P-NaOH	P-HCl
Oxic	0.532*	0.254	0.353*	0.533*	0.253
Anoxic		0.584*	0.611*	0.383*	-0.005
P-Total			0.417*	0.593*	-0.844*
P-NH$_4$Cl				0.348*	0.241
P-NaOH					-0.130

Note: All data were logarithmically transformed (i.e., natural logarithm). Asterisks indicate significant correlations at the 5 percent level or less.

P-HCl, suggesting that loosely bound P and iron- and aluminum-bound P increase while calcium-bound P decreases with increasing total P content in the sediment. Rates of P release under both oxic and anoxic conditions were correlated with P-NH$_4$Cl and P-NaOH, but not with P-HCl (Table 2). These relationships suggested that loosely bound P and iron- and aluminum-bound P sediments contribute to P release from the sediments under both oxic and anoxic conditions in Lake Pepin. However, regression analysis of P release from sediments versus P-NaOH [ln oxic P release = 0.39 ln(P-NaOH) + 1.76; ln anoxic P release = 0.16 ln(P-NaOH) + 2.90] explained only 28 percent and 15 percent of the variance, respectively. These relatively poor relationships suggest that other sediment variables may be of greater importance in governing P release from sediments in Lake Pepin.

Oxic and nearly isothermal conditions occurred at all peeper deployment stations, mean water temperature was about 22.9 °C at a depth of 10 cm above the sediment-water interface, and mean pH in the bottom waters ranged from 8.3 to 8.8. Steep gradients in SRP, determined from sediment peepers, existed between the porewater and the overlying water column at all stations during the summer months of 1992 (Figure 2). At station UM779.0, for instance, mean SRP in the overlying water increased from 0.121 mg/L to 0.283 mg/L over an interval of 7 cm above the sediment surface. Relatively high SRP just above the sediment-water interface suggests the accumulation of sediment-derived P in the water column. In the porewater at station UM779.0, SRP increased by greater than one order of magnitude (4.066 mg/L), just 1 cm below the sediment-water interface. Porewater SRP also increased with increasing depth of the sediment, often attaining values >6.0 mg/L at sediment depths greater than 6 cm (Figure 2). Mean Fickean diffusional fluxes for P ranged from 2.4 to 7.1 mg m^{-2} d^{-1} in the main basin of the lake and were not
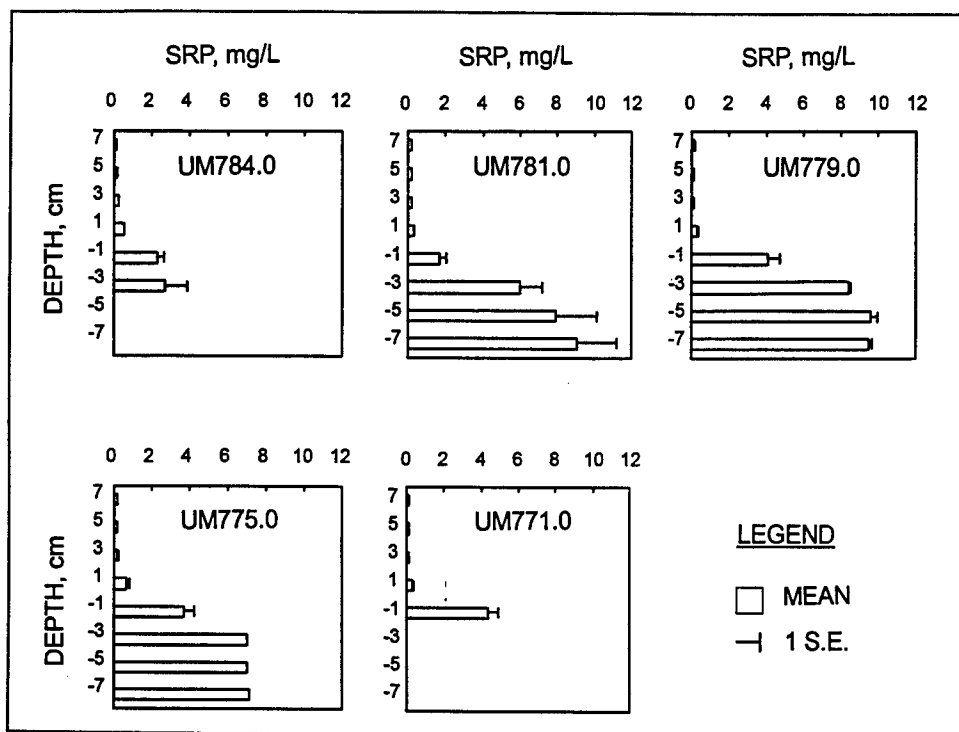
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Figure 2. Variations in mean (±1 S.E.; n = 3) soluble reactive phosphorus concentrations in the porewater of the profundal sediments and overlying water column at several stations in Lake Pepin (Discrepancies in depth (i.e., stations UM784.0 and UM771.0) resulted from difficulties in inserting peepers uniformly into the sediment)

significantly different from those rates determined under oxic conditions and similar temperatures in laboratory incubation systems (Table 3).

Results indicate that P release from the sediments of Lake Pepin is high, even under oxic conditions and lack of thermal stratification. Relatively high pH values (i.e., >8), commonly observed in Lake Pepin, may play a role in P release under oxic conditions. Production of hydroxyl ions during photosynthetic activity may enhance P release from oxic sediments via ligand exchange on the surfaces of iron hydroxides (Drake and Heaney 1987, Boers 1991, Jenson and Anderson 1992). The P-NaOH fraction, which is prevalent in the sediments of Lake Pepin, is most strongly affected by high pH values and potential ligand exchange (Boström 1984).

The development of vertical gradients in SRP above the sediment surface in Lake Pepin during the summer, even under oxic conditions, coincides with the observation of high rates of P release from the oxic sediment, suggesting the accumulation of sediment-derived P in the water column. Thus, internal P loading from the sediment potentially plays an important role in the P economy of Lake Pepin. The high measured rates of internal P loading from sediments reported here for oxic, as well as anoxic, conditions have important implications for P dynamics in Lake Pepin. Particularly during periods of low summer inflow, as in 1988, internal P loading from sediments can account for 11 percent and 33 percent percent of the total daily P load to the system under

Table 3
Direct Comparison of Mean (±1 S.E.) Rates (mg m^{-2} d^{-1}) of P Release from the Sediment Measured In Situ with Sediment Peepers (Fickean Diffusional Fluxes) and In Vitro with Laboratory Incubation Systems Under Oxic and Anoxic Conditions

Station	Peeper Rate	Lab Oxic Rate	Lab Anoxic Rate
784B	b[1] 3.1 (1.2)	b 2.7 (0.3)	a 15.8 (--)
781B	b 2.4 (0.6)	b 3.5 (0.5)	a 18.0 (2.5)
779B	b 6.6 (1.0)	b (3.0) (0.3)	a 13.3 (2.3)
775B	b 5.3 (0.8)	b 2.9 (0.3)	a 14.0 (3.4)
771B	b 7.1 (0.8)	b 7.8 (1.5)	a 21.8 (1.6)
OVERALL	b 4.9 (0.6)	b 3.8 (0.5)	a 17.3 (1.4)

[1] Different letters indicate significant differences at the 5 percent level (analysis of variance).

oxic and anoxic conditions, respectively (Lung and Larson 1994). This internal P source could have a substantial impact on P dynamics in Lake Pepin and thus should be considered when evaluating management strategies for this lake.

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13. ABSTRACT (Maximum 200 words)

This study examined rates of internal phosphorus (P) loading from sediments in Lake Pepin, a natural impoundment located on the upper Mississippi River. Laboratory determinations of rates of P release from the sediment, measured using intact sediment core systems, were very high, with mean values ranging from 3.8 to 15 mg m^{-2} day^{-1} under oxic and anoxic conditions, respectively. Independently determined Fickean diffusional fluxes (mean of 4.9 mg m^{-2} day^{-1}), measured in situ under oxic conditions using sediment peepers, were not statistically different from those rates determined in the laboratory under similar temperature, pH, and oxygen conditions. The dominant inorganic P fractions in the sediments were NaOH-extractable P followed closely by HCl-extractable P. Under both oxic and anoxic conditions, significant correlations existed between rates of P release and the NH_4Cl- and NaOH-extractable P fractions, suggesting that loosely bound and iron- and aluminum-bound sediment P contributed to P release from the sediments in this lake. Correlations between total sediment P and extractable sediment P fractions indicated that loosely bound and iron- and aluminum-bound P increased, while calcium-bound P decreased, with increasing total P content of the sediment. Results suggest that internal P loading from the sediments under oxic as well as anoxic conditions can play a very important role in the P economy of this system.

14. SUBJECT TERMS
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Sediment
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